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THE EFFECT OF TEMPERATURE AND HUMIDITY ON SIZE SEGREGATED TRAFFIC EXHAUST PARTICLE EMISSIONS

Milan Jamriska[1], Lidia Morawska[1*], Kerrie Mergersen[2]

[1)] International Laboratory for Air Quality and Health
School of Physical and Chemical Sciences
Queensland University of Technology
2 George Street, Brisbane Q 4001 Australia

[2)] School of Mathematical Sciences
Queensland University of Technology
2 George Street, Brisbane Q 4001 Australia

[*]Corresponding author
Phone: +61 7 3138 2616; Fax: +61 7 3138 9079; Email: l.morawska@qut.edu.au

ABSTRACT

The formation and behaviour of exhaust emissions is affected by environmental, traffic and meteorological conditions. The understanding of the governing processes and dependency between particles and other relevant parameters, as well as the magnitude of the impacts, is still limited and mostly based on a few laboratory studies. The focus of this work is the effect of temperature (TEMP) and relative humidity (RH) and their interaction on traffic emission particles in the size range of 15-850 nm. The relationship was assessed using a large data set collected over a period of six months at two road sites in Brisbane. A sequence of statistical analyses were designed and applied in order to quantify the relationships, comprising of exploratory correlation analysis to identify pairwise linear associations, factor analysis to assess multivariate effects and nonparametric regression tree methods to more carefully explore interactions. The results show that total particle number concentration was dominated by traffic flow rate and wind speed and to a lesser degree by RH and TEMP. In general, an inverse relationship between temperature and concentration, and a direct relationship between RH and concentration was observed. While TEMP was a dominant parameter for particle concentrations in the size range 15-30 nm, its role diminished and RH emerged as a stronger influence as particle size increased. The observed increase for particle concentrations in the size range 50-150 nm could be associated with particle transfer from a smaller to larger size group due to coagulation and condensation induced growth, as well as an increase in primary (engine) emissions. The significant influence of RH on particles in the 150-880 nm size range could be related to particle growth, changes in hygroscopic properties of traffic emissions and particles originating from sources other than traffic. Decreased combustion efficiency may also contribute to higher emissions of particles in this size range.

Keywords*: exhaust emissions, particle nucleation, airborne particles, coagulation and condensation growth, temperature, humidity*

INTRODUCTION

Vehicle exhaust emissions contain a dynamic mixture of pollutants in gaseous and particle forms. Depending on the place and mechanism of formation, the latter is classified as: (i) primary particles, formed by fuel combustion in the engine, consisting mainly of carbonaceous agglomerates with diameters in the size range from 50 to 1000 nm (i.e. accumulation mode); and (ii) secondary particles, typically hydrocarbons or sulphates formed by nucleation during dilution and cooling of the exhaust after dilution, that are usually smaller than 50 nm (nanoparticles) (Kittelson et al., 1998; Sakurai et al., 2001; Vogt et al., 2003). In the air, after emission, the pollutants undergo many transformations affected by a variety of complex, non-linear and interactive processes, which change their concentration and physical and chemical properties (Kittelson et al., 2000). Some of these processes, such as the formation of new particles by nucleation of gas-phase species and the growth of newly formed particles, are poorly understood. In simple terms, the hot gas-phase materials reach the supersaturation conditions and: (i) nucleate, forming new particles and/or condensing on existing particles (heterogeneous nucleation); (ii) these consequently grow via the condensation processes; and (iii) continue their transformation (as volatile nanoparticles) governed by the environmental conditions of the surrounding ambient air.

Atmospheric conditions, in particular relative humidity and air temperature, are factors known to affect transformation processes (Kittelson et al., 2000; Wehner et al., 2002). Their effect is not only on particle formation from vapour-phase precursors, but also on particle aging and the resulting physico-chemical properties, including size. The current theory of the effect of relative humidity and temperature on particle dynamics can be summarized as follows.

The effect of temperature

Ambient air temperature influences all three stages described above. For constant engine operation conditions, a decrease in ambient air temperature increases the supersaturation ratio (Hinds, 1999) thus resulting in an increase of the nuclei mode particles. Assuming an unlimited supply of the other precursors and maintaining the conditions favourable for particles nucleation, new nuclei mode particles are formed. Similarly, lower temperature increases condensation onto already formed particles causing their growth. Both effects have been observed and characterised in laboratory studies. For example, Abdul-Khalek (1999, 2000), Shi (1999) and Charron (2003) reported an inverse relationship between both dilution air TEMP and nuclei mode particles, and TEMP and growth rate.

The effect of relative humidity

Several studies, for example Chan (1996), Kubesh (1997), McCormick (1997) and references therein, have indicated an effect of very high humidity conditions on the combustion process itself, through increased formation of particles in the combustion chamber. Higher moisture content effectively reduces the air density causing a decrease of the oxygen content in the air, thus influencing the air-to-fuel ratio of the combusted mixture. Combustion of a fuel-rich and oxygen-lean mixture decreases engine combustion efficiency, which results in the higher emission rates of soot particles, HC and other unburnt fuel compounds forming primary particles predominantly in the accumulation mode.

Water vapour influences the processes affecting the emissions leaving the exhaust. High moisture content in the air contributes to new particle formation (nuclei mode) and also particles' growth (nuclei mode and primary particles). In both cases this leads to changes in particle size distribution. An increased formation rate of nuclei mode particles for higher relative humidity was reported for example by Abdul-Khalek (1999), Mathis (2004) and Kim (2002). Although fresh primary vehicle emissions are predominantly hydrophobic (Weingartner et al., 1997) they could become hygroscopic under high humidity conditions (>90%) (Weingartner et al., 1995) due to adsorption of organic materials coating particle surfaces (Weingartner et al., 2000; Lammel and Novakov, 1995).

Only a handful of studies have investigated the effect of environmental conditions on traffic emissions. For example, Abdul-Khalek (1999) studied the effect of TEMP and RH under controlled laboratory conditions reporting an increase in nuclei mode formation with decrease of temperature and increase of the RH of the dilution air. At lower temperatures the supersaturation of gas-phase exhausts is increased, causing an increase in formation of the nuclei mode particles. According to the classical nucleation theory, the process includes H_2SO_4 and water vapour (Seinfeld and Pandis, 1998; Hinds, 1999), therefore increasing air humidity effectively increases the supply of one of the reacting components. Both processes result in a higher concentration of nuclei mode particles. A similar conclusion was reached by Kittelson (2004) who studied the effect of temperature on nuclei mode formation in a vehicle chasing experiment. Higher concentration of nanoparticles formed during dilution was observed at lower ambient temperatures (Kittelson et al., 2000 and 2004; Shi and Harrison, 1999; Shi et. al., 1999; Abu-Allaban et al., 2002). Yao et al. (2006) also reported that there is some relationship between the particle number concentrations emitted from on road vehicles and temperature and relative humidity.

Despite these few reported studies on this topic, a comprehensive, quantitative understanding of the impact of humidity and temperature on particle post-emission processes under real environmental conditions is still lacking. The importance of developing a good understanding in this area stems from the impact of particles on human health and the environment, and the need for better prediction of particle characteristics for exposure and risk assessments.

The objective of this study was characterisation of the effect of relative humidity and temperature on the size segregated ambient air particles dominated by traffic emissions. A large set of data was collected at two road sites with different traffic, topographical and meteorological conditions. A sequence of statistical methods was pre-determined to allow exploration and quantification of the effects of interest and their interaction. First, bivariate and partial correlation analyses were used to identify pairwise associations between variables governing particle characteristics. Second, multivariate linear relationships between these variables were evaluated through factor analysis. Finally tree regression was adopted to further deconvolve the interacting relationship between relative humidity and temperature for different particle sizes. This sequenced approach allows postulation about the link between the observed effects and possible causal physico-chemical processes.

EXPERIMENTAL

Continuous measurements of particle characteristics, meteorological conditions and traffic flow rate were conducted at two road monitoring sites from Sept 1998 to Jan 1999 (Tora St) and from June to Nov 1999 (Ipswich Rd), and also at an urban background air monitoring station (QUT). The measurements were conducted as part of a larger on-road study focused on derivation of vehicle emission factors. The results, together with a detailed description of the study design, are presented elsewhere (Jamriska and Morawska 2001; Morawska et al., 2004). Below is a brief summary of the experimental setting of the study.

Monitoring sites

The monitoring site at Tora St, located about 10 km from the Brisbane Central Business District (CBD), represents typical freeway traffic conditions (two lanes in each direction) with the majority of vehicles travelling on the South East Freeway at a steady speed of approximately 100 km h^{-1}. Due to the site location it could be assumed that the cars' engines operated in a steady temperature mode. The road is flat in this area and represents a semi-open, street canyon type with the height of the walls about 5 m.

The Ipswich Rd site, which is about 3 km from the CBD in a high urban density area, represents typical urban traffic conditions with three lanes in each direction, and the majority of vehicles travelling in a stop-start mode between two sets of traffic lights for pedestrian crossings at a maximum speed of 60 km h^{-1}. The road is flat and the site could be described as a street canyon as the road passes between buildings of height up to five levels. The reference site was the Air Monitoring and Research Station operating at the Queensland University of Technology (QUT), located at the Brisbane CBD about 10 and 3 km, respectively from Tora St and Ipswich Rd. While ideally the reference and the measurement sites should have been close by, it would have been impossible within the scope of the project to duplicate the existing, continuously monitoring reference site equipped with the advanced instrumentation for particle monitoring. Extensive tests were conducted to establish the relationship between background concentrations measured at QUT and those at the sampling sites (Morawska et al., 2004).

Measurements of Particle, Meteorological and Traffic Parameters

The monitoring instrumentation was housed in an air-conditioned cabinet located on bridges across the traffic routes. Both the sampling air and the sheath air for the SMPS were taken form outside of the air-conditioned cabinet. Tubes were suspended 3 m from the bridges to provide particle concentration (Jamriska and Morawska, 2001). Scanning Mobility Particle Sizers consisting of Electrostatic Classifiers (EC TSI model 3071A) and condensation particle counters (CPC TSI models 3010 and 3022) were used for the measurements of particle number size distribution and concentration in the 15-880 nm size range. SMPS operated in a continuous mode with one measurement taken over a period of 5 minutes. The SMPS was calibrated prior to the measurements using a known size aerosol produced from a TSI Condensation Monodisperse Aerosol Generator (Model 3475), and the results were corrected for particle losses in the sampling lines. Overall about 8500 complete records were collected for each monitoring site, with occasional gaps in monitoring caused by the instrument’s maintenance or unavailability.

Continuous monitoring of air temperature, humidity, and rainfall were conducted at QUT with time resolution of 30 minutes. It was assumed and latter validated that QUT temperature and humidity data could be used as a good approximates for the road sites.

Traffic flow rate data were obtained for both sites from Queensland Main Roads. Traffic speciation data were also collected at intermittent intervals for four days at Tora St and Ipswich Rd by video taping traffic and then analysing the tapes to obtain information on selected vehicle categories.

Data Analysis

The following parameters were used in data analysis: (i) particle size distribution (PSD) and number concentration; (ii) traffic parameters, including traffic flowrate (TRAF); and (iii) meteorological characteristics including wind velocity (WSPD), relative humidity (RH), temperature (TEMP) and rainfall.

Based on the particles' spectral properties and understanding of modal distributions, the overall range of 15-880 nm was divided into four size classified intervals: (i) 15-30 nm; (ii) 30-50 nm; (iii) 50-150 nm; and (iv) 150-880 nm; with the corresponding number concentration in these intervals denoted as N_{15-30}; N_{30-50}; N_{50-150} and $N_{150-880}$, respectively. While the exact division may be arbitrary, the sub-classes relate to: (i) the nuclei mode particles; (ii) Aitken mode (which was considered to be associated primarily with petrol engine emissions); (iii) Lower Accumulation mode I (associated primarily with diesel engine emissions); and (iv) Higher Accumulation mode II (associated primarily with aerosol transformed from smaller size groups and linked to the aged emissions and/or aerosols originating from other than traffic exhaust sources).

All the experimental data were screened for validity and completeness. Screening involved statistical elimination of any corrupt data, identification and assessment of any extreme values and characterisation of data distribution, in particular normality (Yu et al., 2004). To exclude the effect of rain, only data with a zero rainfall were considered. Only the subsets containing a complete set of data (i.e. particle, traffic and meteorological parameters) were used for the analyses.

Statistical methods

Correlation Analyses

The degree of linear association between each pair of variables was assessed by Pearson and Spearman's Rank correlations. In particular, the main independent variables individually associated with particle total and size segregated concentration were identified by larger positive or negative correlation coefficients. The effect of RH and TEMP (independent variables) on particles' size segregated concentration (dependent variables) was estimated indirectly, assuming that a strong association between the two parameters could be indicated by an increase in correlation as compared to a weak or nonexistent relationship. For example, if TEMP is associated with an increased rate of formation of particles in the nuclei mode (N_{15-30}) while the larger particles are not affected or are affected to a lesser degree by TEMP, then an increased correlation $r_{N15-30,}$

$_{TEMP}$ as compared to $r_{N150\text{-}880,\ TEMP}$ is expected. Similarly, a stronger effect of RH on larger particles is expected to result in $r_{N150\text{-}880,\ RH} > r_{15\text{-}30,\ RH}$.

Since TEMP and RH are strongly dependent, partial correlations were also calculated to identify the impact of these two variables on $N_{D1\text{-}D2}$ (particle concentration within D_1–D_2 diameter size range) after controlling for TRAF, WSPD and RH; and TRAF, WSPD and TEMP. The difference between the values of bivariate and controlled correlation indicates an effect of the control variables (Blalock, 1961).

A Bonferroni correction was employed to account for the multiple correlation tests undertaken on this single dataset. This sets a higher threshold for claiming statistical significance, to ensure an overall 5% significance level.

Factor Analysis

Factor analysis allows the construction of a new set of independent variables, or factors, based on linear combinations of the original variables. Inspection of the variables combined within factors and their associated weights, as well as a comparison across factors may lend insights into different dimensions of the data. Each of the variables described above was standardized to have mean 0 and variance 1. Letting X_j, $j=1,.., p$ denote the standardized variables, the new factors $PC_i=\Sigma a_{ij}X_j$, $i=1,\dots,n$ were constructed using principal component analysis. In each factor, the a_i's indicate the relative weight of the variable X_i. The relative weight, or loading, of each factor in describing the original data is determined by its eigenvalue. The number of factors, *m*, was chosen using a cutoff loading value of 0.1. This gave an acceptably small residual variance, that is, the proportion of total variance in the *X*'s not explained by the *m* factors.

Tree regression

Classification and regression trees (CART) (Breiman et al., 1984) were used to model the relationship between each of the concentration variables ($N_{15\text{-}880}$, $N_{15\text{-}30}$, $N_{30\text{-}50}$, $N_{50\text{-}150}$, $N_{150\text{-}880}$) and the set of explanatory variables TRAF, WSPD, TEMP and RH. The CART methodology is detailed in the seminal text by Breiman et al (1984) and its implementation in the S-Plus software is described by Clark and Pregiborn (1992). The applicability of CART as a simple tool for describing complex environmental interactions is well described by De'ath and Fabricius (2000) and in a comparison of various modelling approaches, Breiman (2001) gave CART a rating of A+ for interpretability. This nonparametric alternative to classical linear regression allows much easier representation of nonlinear relationships and interactions in the data. Since tree-based models are scale-invariant, no data transformation is required. The analysis proceeds by first identifying a binary split in one of the explanatory variables that leads to the largest separation of the response. This split clusters the data into two more homogeneous groups, and thus forms the first two 'branches' of the tree. Each subgroup is then considered separately, and again split into two by one of the explanatory variables. Splitting continues until specified criteria are satisfied. In the present analysis, the two criteria were a minimum number of 500 observations in a subgroup and a minimum node deviance of 0.2 (optimal recursive shrinking, with the shrinkage parameter (1:10)/(20:11). The results of the CART analysis are represented as a tree, with branches indicating the classification rules and terminal nodes representing the average concentration for particles at the given size group (N_{D1-D2}).

RESULTS AND DISCUSSION

In order to investigate the effect of ambient air temperature and relative humidity on size grouped particle concentrations, the following steps were taken: (i) identification of the main parameters; (ii) semi-quantitative characterisation of the effect of the identified parameters on PSD; and (iii) interpretation of the observed trends in relation to the relevant physical processes and mechanisms.

Descriptive statistics of the main parameters measured at both monitoring sites are presented in Tables 1(a) and 1(b). The results can be summaries as follows.

Traffic flow rate

Hourly averages of traffic flow rate presented in Figure 1a show a diurnal variation with an increase during the morning and afternoon peak hours, around 7:00 AM and 5:00 PM, and maximum of about 1.4 car s^{-1}. While the median values of about 0.5 car s^{-1} are similar for both sites, traffic fleet composition and driving mode (as explained above) differ. At Tora St, the fleet consist of approximately 90% gasoline and 10% diesel powered vehicles, while at Ipswich Rd it was 80% and 20%, respectively.

Meteorological conditions

Hourly averages of wind speed are presented in Figure 1b. In general, wind speed measured at both sites was approximately normally distributed (skewness 1.4 and 1.1) with median 1.4 and 1.6 m s^{-1} for Tora St and Ipswich Rd, respectively. The normal wind speed NWSPD (wind speed perpendicular to road direction), followed in general the same trends as observed for WSPD with median values of about 0.5 m s^{-1}.

The time series of average TEMP and RH measured at QUT during monitoring at both sites are presented in Figure 1c. The series represent a typical daily pattern with the temperature maximum at around noon, which is accompanied by minimum RH. The TEMP and RH during measurements at Tora St ranged from 10 to 35^{o}C with median of 22^{o}C, compared to the range of 6-27^{o}C and median of 17^{o}C for Ipswich Rd. The median RH values were about 70% and 80% for Tora St and Ipswich Rd, respectively. The relative humidity during monitoring at Ipswich Rd was on average 10% higher compared to Tora St. The differences are associated with the fact that the measurements at Tora St were conducted mainly during summer (Oct-Jan) and at Ipswich Rd during winter/spring (June-Sept). The moderately strong inverse relationship observed between relative humidity and temperature during monitoring periods is presented in Figure 2. The corresponding correlation coefficients were -0.63 and -0.72 for Tora St and Ipswich Rd, respectively.

Particle characteristics

Particle characteristics measured at both sites are presented in Tables 1(a) and 1(b). In general, the concentration levels at Tora St were higher by a factor of about two. The median value for $N_{15\text{-}880}$ was 2.1×10^{4} compared to 1.2×10^{4} particle cm^{-3}. The nuclei mode $N_{15\text{-}30}$ particles represented about 50% and 36% of the total for Tora St and Ipswich Rd, respectively. For Aitken mode N_{30-50} particles, the fractions were 22% and 25%. The differences in particle concentrations and size distribution between Tora St and Ipswich Rd could be attributed to the differences in driving modes, traffic fleet compositions and site topography.

Correlation analyses

Bivariate Pearson correlations are presented in Table 2. Most of the variables were significantly correlated at the 1% level, due to the large number of observations. TRAF and WSPD were most strongly correlated with particle concentration levels at both sites ($0.3<|r_{TRAF}|<0.7$). The effect of WSPD is similar at both Tora St and Ipswich Rd, whereas TRAF is more dominant at Ipswich Rd. For example, the correlation coefficient between N_{15-880} (total concentration) and TRAF is almost twice that observed for Tora St (r~0.43 compared to 0.23). This may be attributed to the differences in the sites' geometry and wind and traffic turbulence induced dilution. Stronger and more rapidly changing dilution at Tora St (higher traffic speed, semi-open topography) could mask the effect of individual vehicles, causing lower correlation between the traffic flow and measured particle number concentration.

The correlations between each of RH and TEMP and particle concentration levels are also statistically significant but relatively weak ($0<|r|<0.3$) as seen in Figures 5 and 6. Moreover, the strength and direction of the association varied substantially across the two sites and for different particle sizes. At the Tora St site, a strong negative association ($r<0.10$, $p<0.01$) was observed between TEMP and the smallest size range (N_{15-30}), coupled with a strong positive association ($r>0.10$, $p<0.01$) with RH in the largest size range ($N_{150-880}$). Conversely, at the Ipswich Rd site strong positive associations were observed between TEMP and both the smallest and largest size ranges, coupled with a strong negative association between RH and the smallest size range.

As summarised in Table 3, the Bonferroni analyses confirmed the different effects of TEMP and RH across three distinct size classes, 15-30 nm, 30-50 nm and above 50 nm. Groups that are represented as connected do not show statistically significant differences at the 5% level. In addition, the partial correlations between N_{D1-D2} and TEMP and N_{D1-D2} and RH showed in general the same trends as the bivariate correlations but were substantially higher after controlling for the other independent variables. The effect of TEMP was dominant for the lower size ranges (N_{15-30} and N_{30-50}) while RH seemed to have most influence on the larger size ranges (N_{50-150} and $N_{150-880}$).

Factor Analysis

The results for both sampling sites showed that the first three principal components explained more than 85% of the total variation in the original data, with PC1, PC2 and PC3 contributing approximately 50%, 23% and 13%, respectively.

The highest loadings in PC1 were associated with meteorological parameters (WSPD, TEMP, RH) and traffic flowrate (TRAF). TEMP and RH had similar absolute loadings but with opposite signs, reflecting their strong inverse relationship. Particle concentration (for all size ranges) and WSPD showed the highest loadings in PC2 and, as expected, opposite signs. PC3 for Tora St was dominated by WSPD and TEMP, again indicating an inverse relationship between these two variables since increased wind speed results in lower air temperature. A similar trend was detected at Ipswich Rd, however in addition to WSPD and TEMP, the other variables showed substantial (>0.1) loadings. This indicates a more complex relationship between Ipswich Rd data compared to Tora St.

Overall, the meteorological and traffic parameters dominated the first principal component and thus contribute most to the explanation of the variation in the dataset. Particle concentration and wind speed dominated the second component. RH and TEMP alone explained a substantial proportion of the total variance and appear to act in opposite directions. The PCA does not allow for further separation of the RH and TEMP effects. This motivates the use of the CART analysis, described in the next section.

Tree Regression

CART analysis of the effect of TEMP and RH on size segregated particle concentration provided the following observations.

Particles in the entire size range $N_{15\text{-}880}$

Particle concentration $N_{15\text{-}880}$ was dominated by a direct relationship with traffic flowrate indicating that increases in TRAF were related to the increase in concentration. The second most dominant parameter was WSPD, which showed an inverse relationship with concentration, i.e. higher wind speed was associated with lower $N_{15\text{-}880}$. This can be expected as higher WSPD means higher dilution causing a decrease in particle concentration. The tree-regression model also indicated a dependency of $N_{15\text{-}880}$ upon

RH, with the increases in $N_{15\text{-}880}$ being associated with lower TEMP and higher RH. As seen from the regression tree for Tora St in Figure 3a, the highest concentration $N_{15\text{-}880}$ (~50,000 particle cm^{-3}) was observed for TEMP <17.9°C (TRAF>0.15 car s^{-1} and WSPD<1.7 m s^{-1}). $N_{15\text{-}880}$ increased for larger RH, with a critical split value for Tora St at 72.7%**.** The effect of TEMP on Ipswich Rd data, while showing the same trend, was less pronounced and was observed only for low traffic (TRAF<0.67 car s^{-1}) and low WSPD (<0.87 m s^{-1}) conditions. The split TEMP value was about 14.7°C as presented in Figure 3b. The effect of RH on $N_{15\text{-}880}$ at Ipswich Rd was not observed. The discrepancy could be attributed to traffic and topography differences between the two sites. This analysis indicates a subtle interactive relationship between particle concentration, TEMP and RH in this size range.

Nuclei mode $N_{15\text{-}30}$

Since total concentration is dominated by particles in the 15-50 nm size range, similar trends to those observed for $N_{15\text{-}880}$ could be anticipated for $N_{15\text{-}30}$ (Nuclei mode) and $N_{30\text{-}50}$ (Aitken mode) particles. As can be seen from Figures 4a (i) and 4b (i), particle concentration in the nuclei mode for both sites is dominated by TRAF and WSPD and to a lesser degree by TEMP (Tora St). Higher $N_{15\text{-}30}$ levels are observed for lower temperature and for relatively low wind speed (WSPD < 2-2.4 m s^{-1}). At Tora St the TEMP effect is very dominant, with a split due to TEMP at the 2nd level of the tree with a critical value at about 16.9°C. Additional branching due to TEMP was observed at the 4th and 6th levels of the tree for temperature values 21°C (WSPD<2.4 m s^{-1}) and 27°C (WSPD<2.4 m s^{-1} and TRAF>0.32 car s^{-1}). At Ipswich Rd the effect is less pronounced, with splits occurring at the 3rd level of the tree (Figure 4b (i)) for TEMP values at about 19.6-21°C.

At both sites, low TEMP is associated with an increase of nuclei mode particles. This could be due to increased rates of gas–to-particle conversion (homogeneous nucleation) and condensation on existing aerosols (heterogeneous nucleation) occurring at lower temperatures. It is likely that although the initial size of nuclei mode particles was below the measured size range, the growth rate and residence time were sufficient for these particles to increase their size into the 15-30 nm size range. The effect of RH on $N_{15\text{-}30}$ was not observed.

Aitken mode $N_{30\text{-}50}$

Tree-regression applied to $N_{30\text{-}50}$ shows similar trends to those observed for $N_{15\text{-}30}$ for Tora St data, however these are less pronounced. Splits due to TEMP occurred at the 3rd level (TEMP~18.1°C) and 5th level (25°C) of the tree for Tora St, for WSPD<1.7 m s^{-1}, WSPD<3.2 m s^{-1} and TRAF>0.39 car s^{-1}. The branching at higher TEMP values occurred for relatively higher TRAF values and low to moderate wind speed (WSPD<3.2 m s^{-1}). The RH effect for Tora St, although observed, occurred at the 5th level. An interpretation of this result could be that the $N_{30\text{-}50}$ range is affected mainly by primary emission particles from gasoline vehicles (Ristovski et al., 1998). Since the effect occurs for TRAF>0.28 car s^{-1}, this indicates that the emissions themselves may be affected by RH, with an increase observed for more humid conditions. It is possible that this was due to less efficient fuel combustion, resulting in higher emissions of primary particles. If correct, the effect should be more pronounced for the next size range N_{50-150}, as it is known that an increase in RH may result in an increased emission due to deterioration of combustion efficiency in the internal combustion processes(Chan and Zhu, 1996; Kubesh and Podnar, 1997; McCormick et al., 1997). As presented below, this was indeed the case. The results are also indicative of the interactive nature (in terms of statistical models) of TEMP and RH, since both parameters are present in the tree regression for N_{30-50} and larger size groups. The effect of TEMP and RH on N_{30-50} for Ipswich Rd data was not observed.

Lower Accumulation mode I N_{50-150}

Tree regression with N_{50-150} as the response parameter showed that TRAF is the most dominant parameter affecting data structure for both sites; however for Tora St, the RH is the second most important parameter. The critical split values were 92.6% (TRAF<0.33 car s^{-1}) and 77.9% (TRAF>0.33 car s^{-1}). Wind speed is the third most dominant parameter. The importance of RH as the branching parameter could be associated with decreased efficiency of internal engine combustion processes, resulting in higher emissions of primary aerosols in the accumulation (50-150 nm) mode. Tree-regression for Ipswich Rd for N_{50-150} showed a different pattern compared to Tora St. The N_{50-150} data structure for Ipswich Rd followed, in general, a similar trend to that observed for N_{15-880} (Figure 3b) with increased N_{50-150} values associated with higher TRAF and lower WSPD. The TRAF and WSPD were the most dominant factors, causing branching at the 1st and 2nd levels, respectively (Figure 4b (iii)). TEMP (critical value 10.2°C) caused branching at the 3rd level (TRAF<0.67 car s^{-1}, WSPD >0.71 m s^{-1}). Although less dominant, the effect of RH was also observed at the 4th level, indicating an increase in N_{50-150} for RH>61%. Therefore it can be concluded that at Ipswich Rd, while the effect of TEMP and RH was present, it was less dominant than at Tora St.

Higher Accumulation mode II $N_{150-880}$

For $N_{150-880}$ tree-regression the effect of RH increased, especially for Tora St, where it become the most dominant factor, overtaking the role of TRAF and WSPD. For Ipswich Rd it became more pronounced (compared to N_{50-150}) at the 3rd level of branching. The critical RH values associated with data branching determined by the tree-regression model for Tora St data were about 92% and 73%. As presented in Figure 4a (iv), for RH above 91.9% the $N_{150-880}$ concentration are high even for small TRAF (TRAF<0.095), and are comparable to conditions with TRAF>0.53 car s^{-1} (RH<73% and WSPD<2.8 m s^{-1}). This indicates the presence and the effect of high RH on particles originating from sources other than traffic. For TRAF>0.095 car s^{-1} and RH>92%, the $N_{150-880}$ levels are the highest. For TRAF >0.33 car s^{-1} (i.e. 73 % of median value, Tora St) and RH>73 %, the $N_{150-880}$ are also very high.

In summary, the $N_{150-880}$ at Tora St were strongly affected by RH, with the effect being dominant for high humidity levels, above 92%, and associated with an increase in particle concentration in this size range regardless of the traffic flow rate. This could be associated with an increased growth rate of aerosol from smaller size ranges (<150 nm) into the 150-880 nm range due to the increased effect of condensation; and /or the hydration effect of “normally” hydrophobic aerosols, which for such high RH may become hydroscopic and show an increased water vapour intake, thus resulting in their growth. The results for RH~73% may be linked to the decrease in combustion efficiency and increased primary emissions.

At Ipswich Rd, the $N_{150-880}$ is dominated by TRAF and WSPD. The maximum particle concentrations are for TRAF>0.66-0.90 car s^{-1} and wind speed<1.29 m s^{-1} (i.e. high traffic volume and relatively low winds). The effect of RH and TEMP, which dominated Tora St data, is present but less pronounced. In general, the same features as described for Tora St are observed: the values of $N_{150-880}$ increased for RH above 87%, for low traffic (TRAF<0.66 car s^{-1}) and low WSPD (<0.87 m s^{-1}) conditions. For higher dilution/mixing with WSPD >0.87 m/s, mid-range traffic flowrate (0.30-0.66 car s^{-1}) and RH above 78%, the $N_{150-880}$ increased to approximately 75% of maximum.

CONCLUSIONS

In summary, the CART models, along with the findings from other statistical methods applied, indicate that total particle concentration (15-880 nm) is dominated by TRAF and WSPD and to a lesser extent by TEMP and RH. TEMP significantly influences N_{15-30}, which could be attributed to increased particle nucleation occurring at a low temperature of ambient air. TEMP and RH also affect Aitken mode (30-50 nm) particle concentration, however the effect seems to be less pronounced. RH appears to be an important parameter influencing particles in the lower accumulation mode (50-150 nm), with increased N_{50-150} for higher RH conditions. The effect could be associated with particle growth from smaller size ranges due to condensation and increased emissions of primary (soot) particles caused by reduced efficiency of internal combustion (in the engine). Concentration levels in the higher accumulation mode (150-880 nm) are significantly affected by RH. It is possible that this is related to an enhanced coagulation and condensation effect of RH, as well as the change of hygroscopic properties of the traffic-originated particles and particles from other sources. Decreased combustion efficiency may lead to emissions of particles in this size range as well. The presented results are in agreement with those based on laboratory and a few, of limited-scope, field studies which have been reported so far.

References

Abdul-Khalek, I. S., & Kittelson, D. B. (1999). The influence of dilution conditions on diesel exhaust particle size distribution measurements. SAE Technical Paper Series, 1999-01-1142.

Abu-Allaban, M., Coulomb.W., Gertler, A. W., Gillies, J. A., Pierson, W. R., Rogers, C. F., Sagebiel, J. C., & Tarnay, L. (2002). Exhaust particle size distribution measurements at the Tuscarora Mountain tunnel. Aerosol Science and Technology, 36, 771-789.

Blalock, H. (1961). Causal inferences in non-experimental research. Chapel Hill, NC: UNC Press.

Breiman, L., Friedman, J. H., Olshen, R. A., & Stone, C. J. (1984). Classification and Regression Trees: Wadsworth & Brooks/Cole Advanced Books & Software.

Breiman, L. (2001) Statistical modelling: the two cultures. Statistical Science 16(3), 199-231.

Chan, S. H., & Zhu, J. (1996). Exhaust emissions based air-fuel ratio model (I): Literature reviews and modelling. SAE Transactions, 105(4), 408-417.

Charron, A., & Harrison, R. M. (2003). Primary particle formation from vehicle emissions during exhaust dilution in the roadside atmosphere. Atmospheric Environment, 37(29), 4109-4119.

Clark, L. and Pregiborn, D. (1992) Tree-based models. In Chambers, J. and Hastie, T. (eds). Statistical Models in S. Wadsworth & Brooks/Cole computer science series. Wadsworth & Brooks/Cole Advanced Books & Software.

De'ath, G., Frabricius, K.E. (2000) Classification and regression trees: a powerful yet simple technique for ecological data analysis. Ecology 81(11), 3178-3192.

Hinds, W. C. (1999). Aerosol technology: properties, behaviour, and measurement of airborne particles (2nd ed.). New York: John Willey & Sons.

Jamriska, M., & Morawska, L. (2001). A model for determination of motor vehicle emission factors from on-road measurements with a focus on submicrometer particles. The Science of The Total Environment, 264(3), 241-255.

Khalek, I. A., Kittelson, D., & Brear, F. (1999). The influence of dilution conditions on diesel exhaust particle size distribution measurements. SAE Technical Paper Series, 1999-01-1142.

Khalek, I. A., Kittelson, D., & Brear, F. (2000). Nanoparticle growth during dilution and cooling of diesel exhaust: experimental investigation and theoretical assessment. SAE Technical Paper Series, 2000-01-0515.

Kim, D.-H., Gautam, M., & Gera, D. (2002). Modelling nucleation and coagulation modes in the formation of particulate matter inside a turbulent exhaust plume of a diesel engine. Journal of Colloid and Interface Science, 249(1), 96-103.

Kittelson, B. D. (1998). Engines and nanoparticles: a review. Journal of Aerosol Science, 29(5), 575-588.

Kittelson, D. B., J. Johnson, J., Watts, W., Wei, Q., Drayton, M., Paulsen, D., & Bukowiecki, N. (2000). Diesel Aerosol Sampling in the Atmosphere. SAE, Tech. Paper Ser. 2000-01-2212, 8.

Kittelson, D. B., Watts, W. F., & Johnson, J. P. (2004). Nanoparticle emissions on Minnesota highways. Atmospheric Environment, 38, 9-19.

Kubesh, J. T., & Podnar, D. J. (1997). Humidity effects and compensation in a lean burn natural gas engine. SAE Technical Paper Series, 1997-1278, 33-40.

Lammel, G., & Novakov, T. (1995). Water nucleation properties of carbon black and diesel soot particles. Atmospheric Environment, 29(7), 813-823.

Mathis, U., Mohr, M., & Zenobi, R. (2004). Effect of organic compounds on nanoparticle formation in diluted diesel exhaust. Atmospheric Chemistry and Physics, 4, 609-620.

McCormick, R. L., Graboski, M. S., Newlin.A.W., & Ross, J. D. (1997). Effect of humidity on heavy-duty transient emissions from diesel and natural gas engines at high altitude. Journal of the Air and Waste Management Association, 47, 784-791.

Morawska, L., Jamriska, M., Thomas, S., Ferreira, L., Mengersen, K., Wraith, D., & McGregor, F. (2004). Quantification of particle number emission factors for motor vehicles from on road measurements. Environmental science and Technology, 39(23), 9130-9139.

Ristovski, Z. D., Morawska, L., Bofinger, N. D., & Hitchins, J. (1998). Submicrometer and Supermicrometer Particulate Emission from Spark Ignition Vehicles. Environmental Science & Technology, 32(24), 3845-3852.

Sakurai, H., et al. (2001). Hygroscopicity and volatility of diesel nanoparticles studied by nano TDMA. Paper presented at the AAAR Annual Conference.

Seinfeld, J. H., & Pandis, S. P. (1998). Atmospheric chemistry and physics: from air pollution to climate change. New York: Wiley.

Shi, J. P., & Harrison, R. M. (1999). Investigation of ultrafine particle formation during diesel exhaust dilution. Environmental Science & Technology, 33(21), 3730-3736.

Shi, J. P., Harrison, R. M., & Brear, F. (1999). Particle size distribution from a modern heavy duty diesel engine. The Science of The Total Environment, 235, 305-317.

Vogt, R., Scheer, V., Casati, R., & Benter, T. (2003). On-road measurement of particle emission in the exhaust plume of a diesel passenger car. Environmental Science &Technology, 37(18), 4070-4076.

Wehner, B., Birmili, W., Gnauk, T., & Wiedensohler, A. (2002). Particle number size distributions in a street canyon and their transformation into the urban-air background: measurements and a simple model study. Atmospheric Environment, 36(13), 2215-2223.

Weingartner, E., Baltensperger, U., & Burtscher, H. (1995). Growth and Structural Changes of Combustion Aerosols at High Relative Humidity. Journal of Aerosol Science, 26, S667-S668.

Weingartner, E., Burtscher, H., & Baltensperger, U. (1997). Hygroscopic properties of carbon and diesel soot particles. Atmospheric Environment, 31(15), 2311-2327.

Weingartner, E., Saathoff, H., Streit, N., Lavanchy, V., Schnaiter, M., Matter, U., & Baltensperger, U. (2000). Hygroscopic behaviour of soot particles coated with oxidation products of [alpha]-pinene. Journal of Aerosol Science, 31(Supplement 1), 987-988.

Yao, X., Lau, N., Fang, M. and Chan, C. (2006) Is on-road particle concentration dependent on ambient temperature and relative humidity? Paper presented to the 7th International Aerosol Concerence.

Yu, R. C., Teh, H. W., Jaques, P. A., Sioutas, C., & Froines, J. R. (2004). Quality control of semi-continuous mobility size-fractionated particle number concentration data. Atmospheric Environment, 38(20), 3341-3348.

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TABLE 1 (a) Descriptive statistics for meteorological, traffic and aerosol parameters measured at Tora St (where FrN is the particles with a given diameter, as a fraction of the total measured concentration).

	Mean	Std Deviation	Median	Percentile 05	Percentile 25	Percentile 75	Percentile 95
TRAF (veh/s)	0.41	0.26	0.45	0.03	0.18	0.57	0.86
WSPD (m/s)	1.68	1.17	1.44	0.31	0.83	2.22	4.03
NWSPD (m/s)	0.70	0.59	0.54	0.05	0.21	1.07	1.85
WDIR (deg)	171	104	142	13	112	264	346
TEMP (C)	21.9	4.4	22.2	14.4	18.8	24.9	28.5
RH (%)	69.6	17.8	68.6	42.5	55.7	85.1	97.0
G.MEAN (nm)	38.1	9.6	36.1	26.9	31.8	42.0	55.9
MODE (nm)	24.3	16.2	18.8	15.1	15.7	25.9	55.2
CMD (nm)	33.5	11.9	30.4	21.8	26.2	36.9	56.9
N15-30 (#/cm^3)	1.35E+04	1.19E+04	1.01E+04	1.60E+03	5.22E+03	1.85E+04	3.62E+04
N30-50 (#/cm^3)	5.92E+03	5.67E+03	4.54E+03	9.03E+02	2.48E+03	7.59E+03	1.53E+04
N50-150 (#/cm^3)	5.47E+03	4.10E+03	4.47E+03	1.20E+03	2.68E+03	7.14E+03	1.31E+04
N150-880 (#/cm^3)	1.17E+03	1.04E+03	8.48E+02	2.35E+02	4.93E+02	1.48E+03	3.13E+03
N15-880 (#/cm^3)	2.56E+04	1.89E+04	2.11E+04	4.79E+03	1.19E+04	3.42E+04	6.11E+04
FrN15-30 (-)	0.50	0.14	0.50	0.25	0.40	0.60	0.73
FrN30-50 (-)	0.23	0.08	0.22	0.12	0.18	0.27	0.36
FrN50-150 (-)	0.24	0.11	0.22	0.10	0.16	0.30	0.44
FrN150-880 (-)	0.05	0.04	0.04	0.02	0.03	0.07	0.12

Number of records N= 8539

TABLE 1 (b) Descriptive statistics for meteorological, traffic and aerosol parameters measured at Ipswich Rd (where FrN is the particles with a given diameter, as a fraction of the total measured concentration).

	Mean	Std Deviation	Median	Percentile 05	Percentile 25	Percentile 75	Percentile 95
TRAF (veh/s)	0.49	0.33	0.49	0.05	0.18	0.78	1.02
WSPD (m/s)	1.81	1.06	1.63	0.44	1.02	2.38	3.83
NWSPD (m/s)	0.56	0.39	0.51	0.05	0.24	0.81	1.22
WDIR (deg)	146	94	176	7	38	185	333
TEMP (C)	16.5	4.6	16.8	8.6	13.0	20.1	23.3
RH (%)	73.3	21.1	78.1	35.5	57.9	92.0	97.9
G.MEAN (nm)	47.7	11.9	45.6	33.2	39.5	53.7	68.9
MODE (nm)	38.5	28.9	28.9	16.8	21.7	42.9	91.4
CMD (nm)	43.8	16.5	39.9	26.9	33.2	50.6	71.2
N15-30 (#/cm^3)	5.97E+03	6.04E+03	4.23E+03	8.55E+02	2.06E+03	7.78E+03	1.66E+04
N30-50 (#/cm^3)	4.00E+03	3.63E+03	2.93E+03	8.64E+02	1.75E+03	5.06E+03	1.05E+04
N50-150 (#/cm^3)	4.58E+03	3.55E+03	3.73E+03	1.06E+03	2.26E+03	5.78E+03	1.10E+04
N150-880 (#/cm^3)	1.29E+03	1.44E+03	9.20E+02	2.17E+02	5.06E+02	1.57E+03	3.61E+03
N15-880 (#/cm^3)	1.55E+04	1.17E+04	1.21E+04	3.70E+03	7.54E+03	2.02E+04	3.79E+04
FrN15-30 (-)	0.36	0.14	0.36	0.14	0.26	0.45	0.58
FrN30-50 (-)	0.26	0.08	0.25	0.14	0.21	0.30	0.38
FrN50-150 (-)	0.32	0.12	0.31	0.15	0.23	0.40	0.53
FrN150-880 (-)	0.09	0.06	0.07	0.03	0.05	0.10	0.18

Number of records N= 8390

TABLE 2 Bivariate Pearson correlation and Sigma value (2-tailed) for TORA St (bottom left) and Ipswich Rd (top right)

IPSWICH Rd / TORA Str	N15-30	N30-50	N50-150	N150-880	n15-880	TRAF	WSPD	NWSPD	TEMP	RH
N15-30	1	.677(**)	.449(**)	.353(**)	.883(**)	.408(**)	-.196(**)	-.148(**)	.138(**)	-.122(**)
	.	.000	.000	.000	.000	.000	.000	.000	.000	.000
N30-50	.653(**)	1	.567(**)	.349(**)	.850(**)	.345(**)	-.225(**)	-.167(**)	.063(**)	-.053(**)
	.000	.	.000	.000	.000	.000	.000	.000	.000	.000
N50-150	.489(**)	.609(**)	1	.557(**)	.767(**)	.291(**)	-.172(**)	-.113(**)	**-.005**	**.012**
	.000	.000	.	.000	.000	.000	.000	.000	.634	.279
N150-880	.373(**)	.358(**)	.721(**)	1	.573(**)	.271(**)	-.077(**)	-.051(**)	.113(**)	-.065(**)
	.000	.000	.000	.	.000	.000	.000	.000	.000	.000
N15-880	.929(**)	.838(**)	.733(**)	.543(**)	1	.429(**)	-.227(**)	-.164(**)	.100(**)	-.081(**)
	.000	.000	.000	.000	.	.000	.000	.000	.000	.000
TRAF	.173(**)	.214(**)	.238(**)	.161(**)	.228(**)	1	.308(**)	.201(**)	.582(**)	-.522(**)
	.000	.000	.000	.000	.000	.	.000	.000	.000	.000
WSPD	-.176(**)	-.136(**)	-.179(**)	-.163(**)	-.195(**)	.467(**)	1	.566(**)	.255(**)	-.218(**)
	.000	.000	.000	.000	.000	.000	.	.000	.000	.000
NWSPD	**-.006**	**.011**	.044(**)	**.007**	**.010**	.485(**)	.432(**)	1	.082(**)	-.220(**)
	.608	**.327**	.000	**.560**	**.376**	.000	.000	.	.000	.000
TEMP	-.165(**)	-.062(**)	**.003**	**-.015**	-.120(**)	.486(**)	.345(**)	.519(**)	1	-.687(**)
	.000	.000	.754	.178	.000	.000	.000	.000	.	.000
RH	.060(**)	**.011**	.092(**)	.126(**)	.067(**)	-.597(**)	-.523(**)	-.525(**)	-.533(**)	1
	.000	**.304**	0.000)	.000	.000	.000	.000	.000	.000	

$N_{Tora\ Str}$= 8539; $N_{Ipswich\ Rd}$= 8390 Correlation is significant at the $^{(**)}$ 0.01 level and $^{(*)}$ 0.05 level (2-tailed).

TABLE 3 Multiple pairwise comparison of partial correlation values using Bonferroni test. Groups connected by a line are not statistically different at 5% significance level.

Concentration vs. RH	TORA Str	N15-30	N30-50	N50-150	N150-880
	IPSWICH Rd	N15-30	N30-50	N150-880	N50-150
Concentration vs. TEMP	TORA Str	N15-30	N30-50	N50-150	N150-880*
	IPSWICH Rd	N15-30	N30-50	N50-150	N150-880*

*correlation between N150-880 and TEMP is at 5% confidence level not significant

Figure 1 (a) (b) (c) Hourly averages of: (a) traffic flowrate; (b) wind speed measured at Tora St and Ipswich Rd; and (c) air temperature and relative humidity measured at AMRS QUT during monitoring at Tora St (Oct-Jan) and Ipswich Rd (June-Oct). The box-whisker plots in (a) and (b) are grand averages, based on all data including week days and weekends.

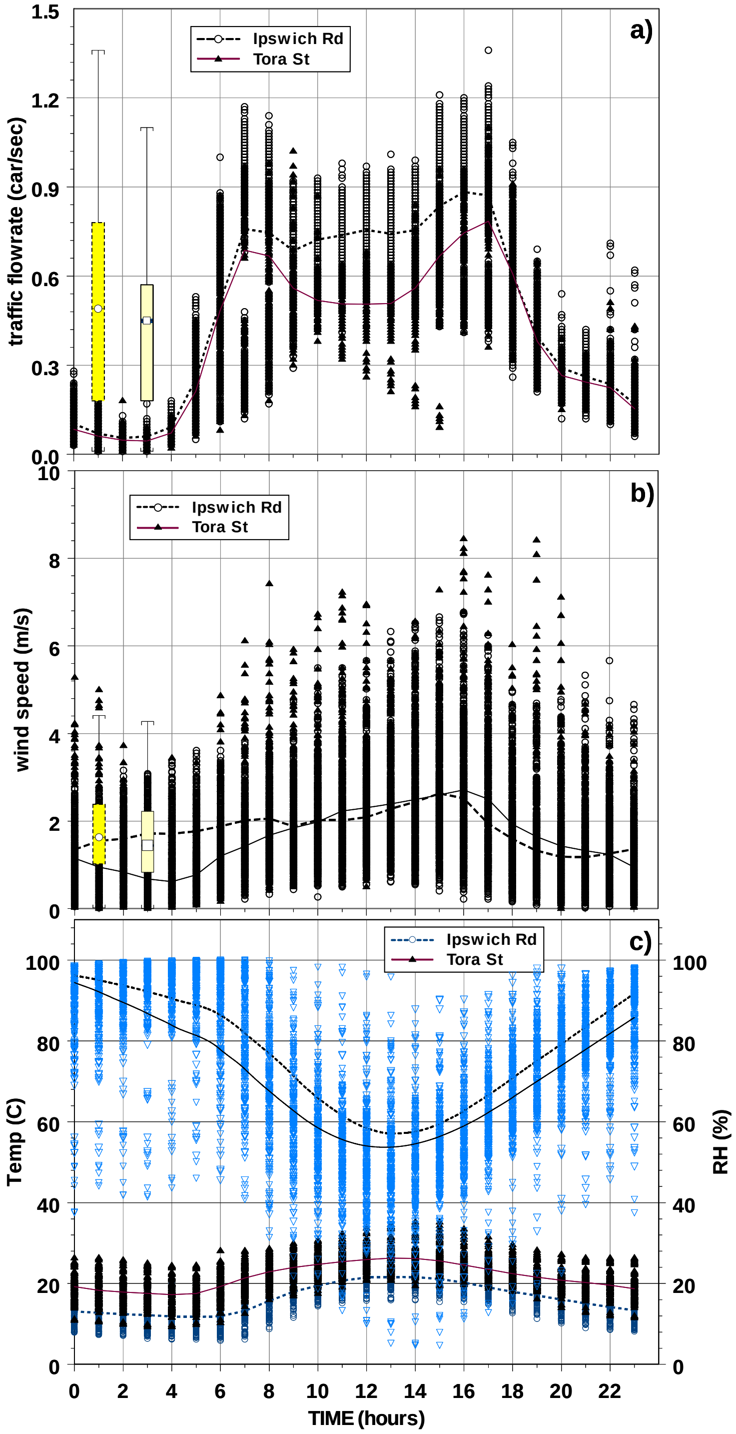


Figure 2 Relationship between relative humidity and air temperature measured at AMRS QUT during the monitoring at Tora St (Oct-Jan) and Ipswich Rd (June-Oct).

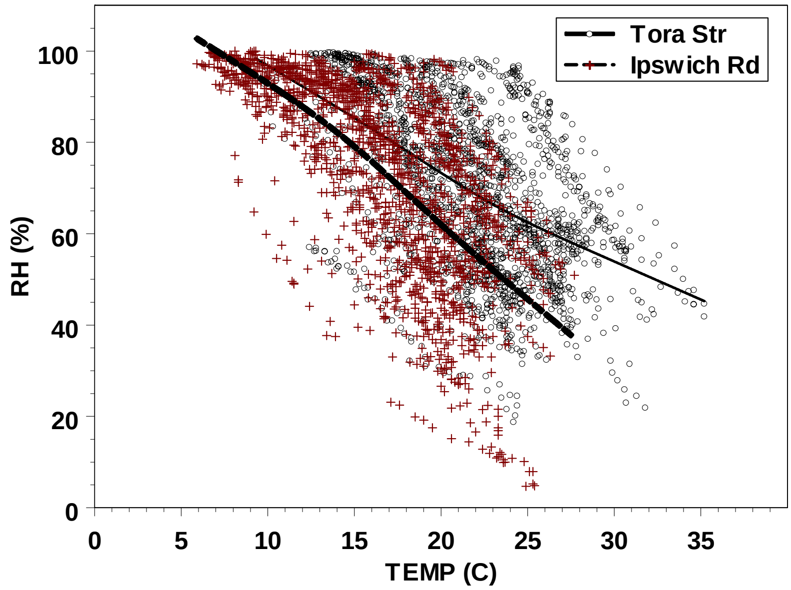


Figure 3 (a) (b) Tree regression model $N_{15\text{-}850}$~TRAF+WSPD+RH+TEMP applied to (a) Tora St and (b) Ipswich Rd data. The value at the node splits the data (eg. Node value = 0.145, therefore the left branch is for all data points with traffic <0.145 and the right branch is for traffic >0.145 car/sec).

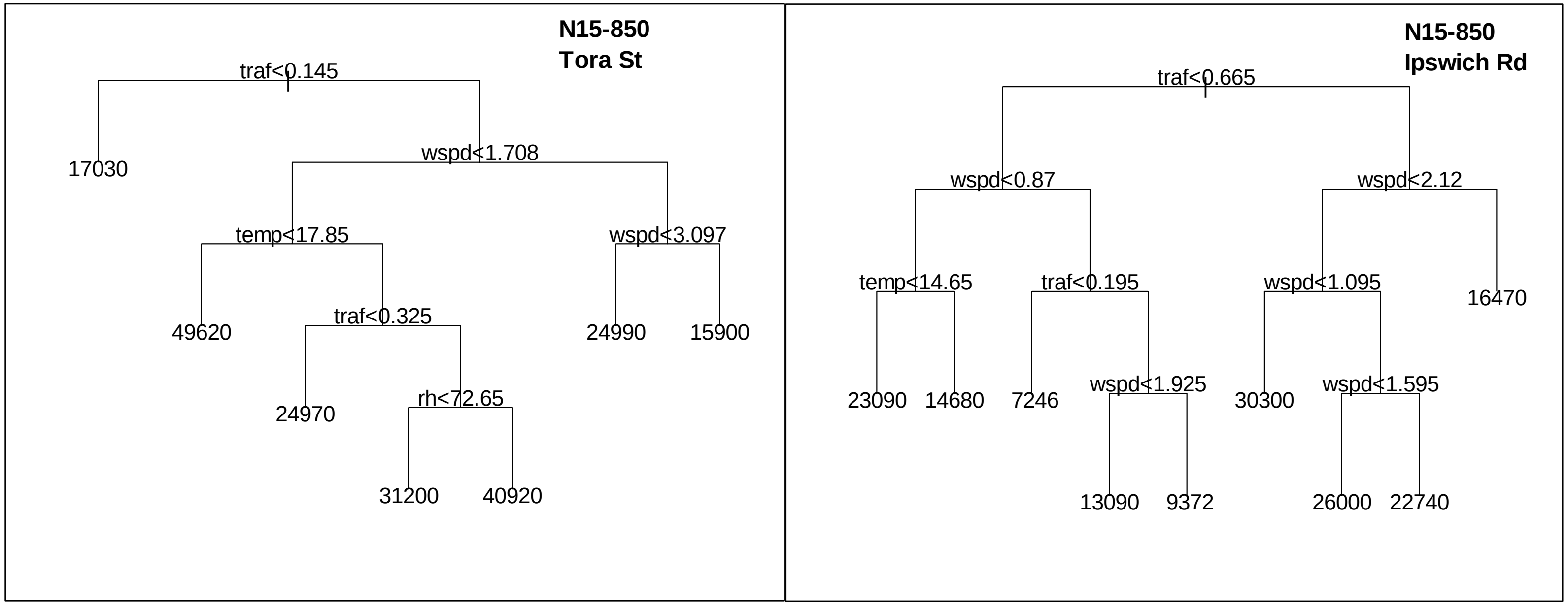


Figure 4a (i) - 4b (iv) Tree-regression models: Response~TRAF+WSPD+RH+TEMP for (a) TORA St; and (b) PAH Data, where the Response values are (i) $N_{15\text{-}30}$; (ii) $N_{30\text{-}50}$; (iii) $N_{50\text{-}150}$; and (iv) $N_{150\text{-}880}$. The value at the node splits the data (eg. Node value = 0.145, therefore the left branch is for all data points with traffic <0.145 and the right branch is for traffic >0.145 car/sec).

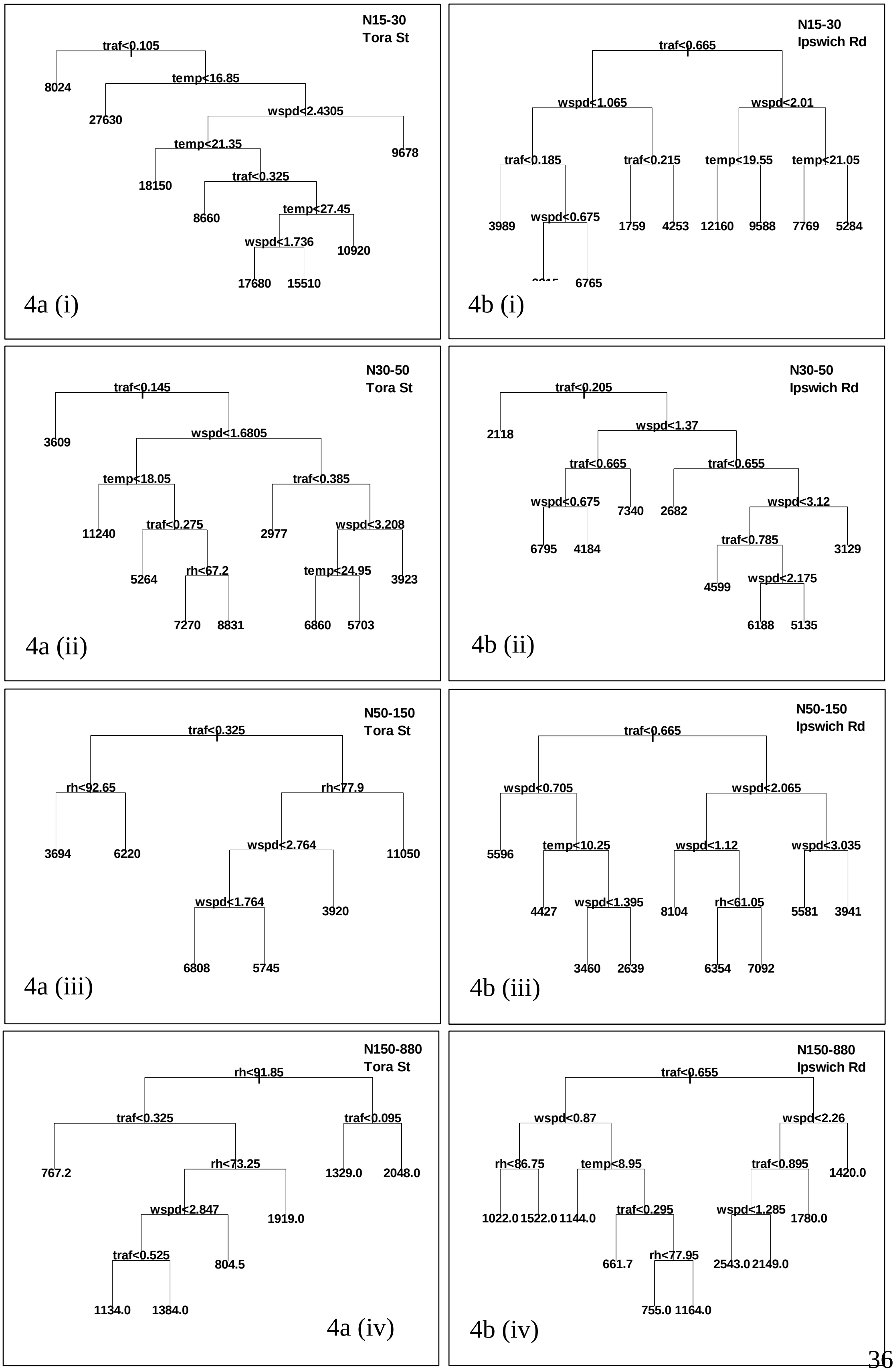
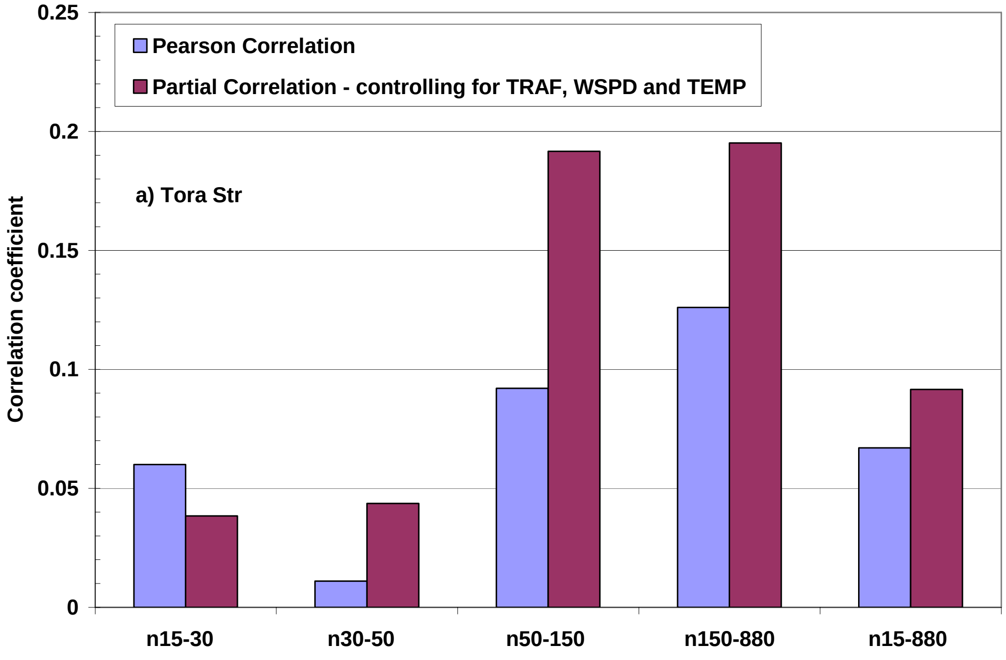


FIGURE 5 (a) (b) Bivariate Pearson and partial correlation between RH and particle number concentration for size segregated groups for: (a) TORA St; and (b) Ipswich Rd. Controlling variables in Partial Correlation: TRAF, WSPD and TEMP.



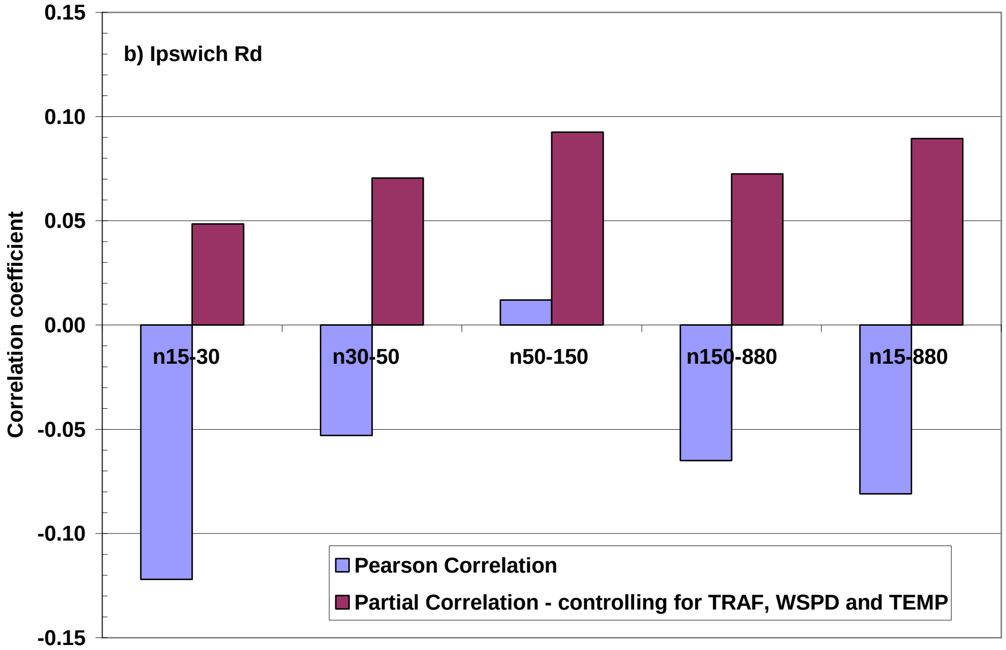


Figure 6 (a) (b) Partial correlation between size segregated particle concentration and: (a) RH (controlling for the effect of TRAF, WSPD, TEMP)
(b) TEMP (controlling for the effect of TRAF, WSPD, RH)